



Oxford Cambridge and RSA

Tuesday 13 October 2020 – Morning

AS Level Chemistry B (Salters)

H033/02 Chemistry in depth

Time allowed: 1 hour 30 minutes

You must have:

- the Data Sheet for Chemistry B

You can use:

- a scientific or graphical calculator
- an HB pencil



Please write clearly in black ink. **Do not write in the barcodes.**

Centre number

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Candidate number

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First name(s)

Last name

StemUp Model Solution

INSTRUCTIONS

- Use black ink. You can use an HB pencil, but only for graphs and diagrams.
- Write your answer to each question in the space provided. If you need extra space use the lined pages at the end of this booklet. The question numbers must be clearly shown.
- Answer **all** the questions.
- Where appropriate, your answer should be supported with working. Marks might be given for using a correct method, even if your answer is wrong.

INFORMATION

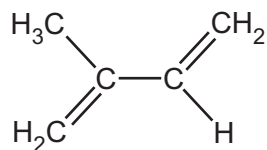
- The total mark for this paper is **70**.
- The marks for each question are shown in brackets [].
- Quality of extended response will be assessed in questions marked with an asterisk (*).
- This document has **20** pages.

ADVICE

- Read each question carefully before you start your answer.

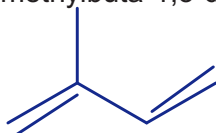
Answer **all** the questions.

- 1 Natural rubber is a polymer of 2-methylbuta-1,3-diene.



2-methylbuta-1,3-diene

- (a) Draw the **skeletal** formula of 2-methylbuta-1,3-diene.

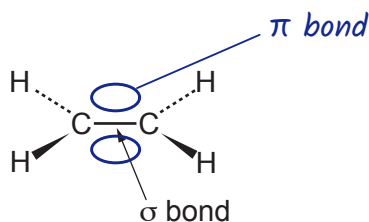


[1]

- (b) The carbon-carbon double bond consists of both a sigma(σ) and a pi(π) bond.

- (i) The diagram of ethene below shows the position of the sigma(σ) bond between the carbon atoms.

On the diagram sketch the shape and position of the pi(π) bond.



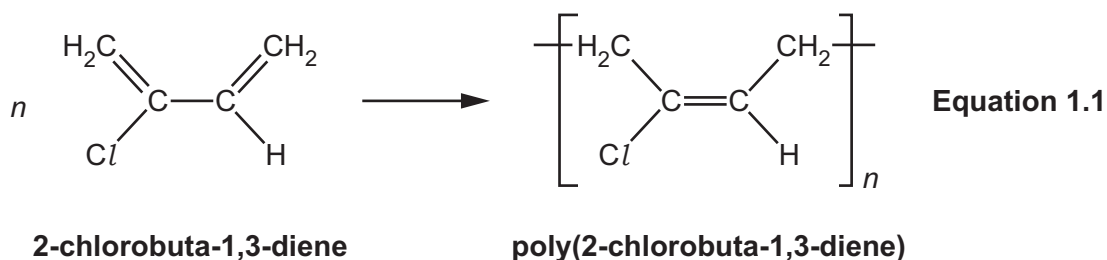
[1]

- (ii) Explain the meaning of the wedge bond ($\blacktriangleright$) in terms of the 3-D shape of ethene.

..It shows a bond pointing towards you: it comes out of (is in front of).....
the plane of the paper..... [1]

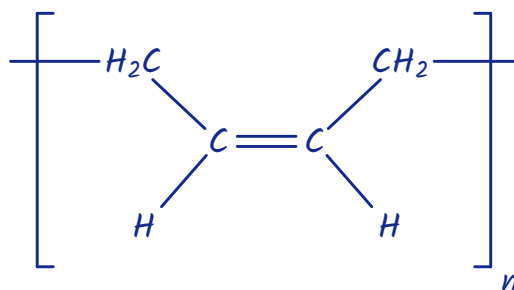
- (c) 2-chlorobuta-1,3-diene, $\text{CH}_2=\text{CClCH}=\text{CH}_2$ is made in industry.

It polymerises, as shown in **equation 1.1**.



- (i) Polymerisation of buta-1,3-diene, $\text{CH}_2=\text{CHCH}=\text{CH}_2$, occurs in the same way to form a synthetic rubber.

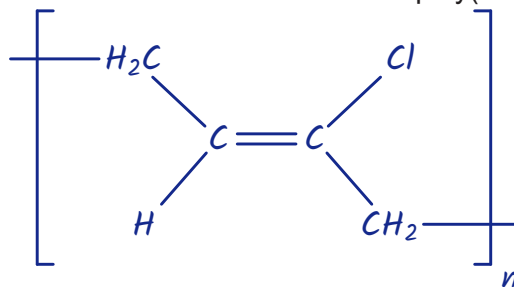
Draw the structural formula for poly(buta-1,3-diene).



[1]

- (ii) The poly(2-chlorobuta-1,3-diene) shown in **equation 1.1** is the *cis*-stereoisomer.

Draw the structure of the *trans*-stereoisomer for poly(2-chlorobuta-1,3-diene).

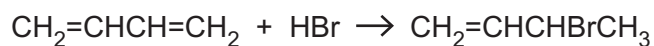


[1]

- (iii) Explain how the two stereoisomers for poly(2-chlorobuta-1,3-diene) occur.

Each carbon atom of the double bond has two different groups attached.
There is no (free) rotation about a carbon-carbon double bond, so the
groups are fixed in position. [2]

(d) The reaction between 1 mol of buta-1,3-diene and 1 mol of hydrogen bromide is shown below.

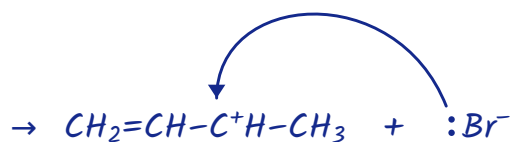
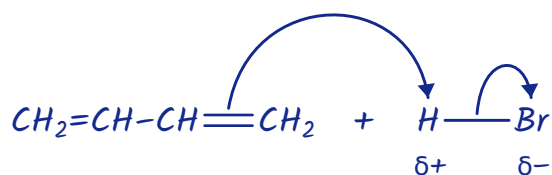


(i) Name the mechanism of this reaction.

Electrophilic addition..... [1]

(ii) Draw the mechanism for this reaction.

Show curly arrows and full and partial charges.



[3]

- 2 Solid barium carbonate, BaCO_3 , is used as a rat poison.

In a rat's stomach, barium carbonate reacts with the hydrochloric acid to produce soluble barium chloride, BaCl_2 , which is poisonous.

- (a) Write an equation for the reaction of solid barium carbonate with hydrochloric acid. Carbon dioxide is produced in the reaction.

Include state symbols.

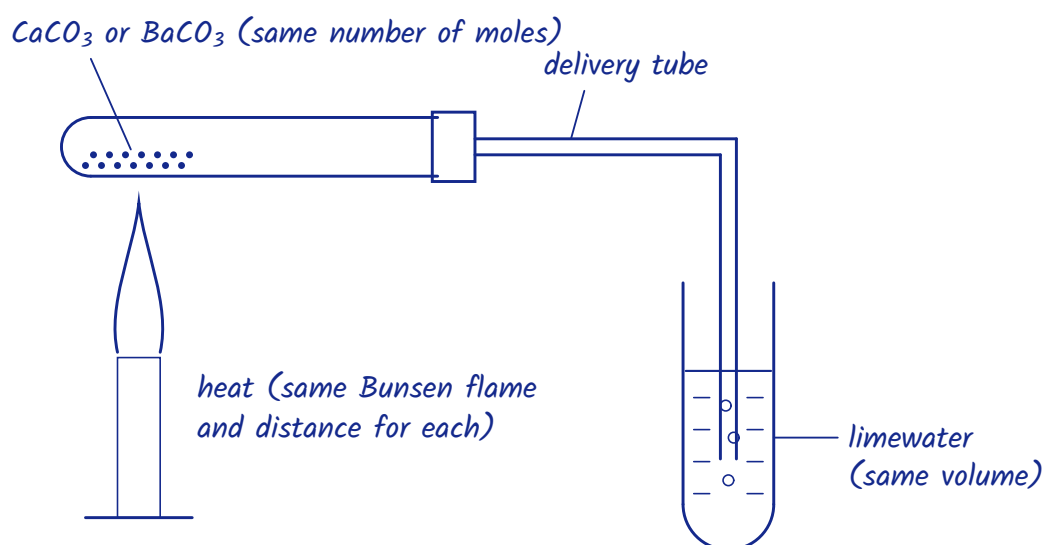


[2]

- (b) (i) Barium carbonate produces carbon dioxide gas when heated strongly. Calcium carbonate is less thermally stable.

Describe an experiment, using limewater, that you could do to show this.

Include a labelled diagram, how you would make it a valid test and what you would observe.



Heat each carbonate in turn and pass the gas given off through
limewater.
Valid test: use the same number of moles (amount) of each carbonate,
the same volume of limewater and the same heating intensity.
Observation: the limewater takes longer to go cloudy (milky) with BaCO_3
than with CaCO_3 .

[4]

- (ii) A student attempts to explain why the thermal stability of the Group 2 carbonates increases down the Group.

The student says it is because the Group 2 metals increase in chemical reactivity down the group. The carbonates of the more reactive elements decompose less easily when heated.

Discuss the student's explanation, giving the correct chemistry where necessary.

The student is incorrect: it is not because the Group 2 metals became more reactive down the Group (it is not to do with reactivity). It is because the Group 2 cations (M^{2+}) get larger, so they have a lower charge density going down the Group. So the cation causes less polarisation (distortion) of the carbonate ion, and the carbonate has greater thermal stability.

[3]

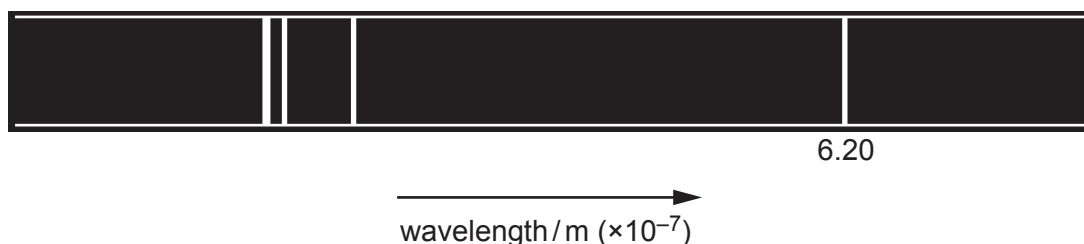
- (c) The presence of calcium in its compounds may be identified using a flame test.

- (i) Give the flame colour for calcium.

Brick red [1]

- (ii) The visible atomic emission spectrum of an element consists of a series of coloured lines on a black background.

A section of this spectrum for calcium is shown in the diagram.



Calcium can also be identified using its atomic **absorption** spectrum.

Describe the appearance of the visible atomic absorption spectrum of calcium and how it is related to the emission spectrum above.

Black lines on a background of the continuous spectrum (all the colours of visible light). The black lines are at the same wavelengths (frequencies) as the coloured lines in the emission spectrum. [2]

- (iii) Calculate the energy change of an electron, in kJ, that causes the line at $6.20 \times 10^{-7} \text{ m}$ in the spectrum of calcium.

$$\nu = c / \lambda = 3.00 \times 10^8 / 6.20 \times 10^{-7} = 4.84 \times 10^{14} \text{ Hz}$$

$$\Delta E = h\nu = 6.63 \times 10^{-34} \times 4.84 \times 10^{14}$$

$$\Delta E = 3.21 \times 10^{-19} \text{ J}$$

$$\text{in kJ: } 3.21 \times 10^{-19} / 1000 = 3.21 \times 10^{-22} \text{ kJ}$$

energy change = ... 3.21×10^{-22} kJ [3]

- (d) A student uses a titration to measure the solubility of calcium hydroxide, $\text{Ca}(\text{OH})_2$.

The student uses a volumetric pipette to transfer 25.0 cm^3 of a saturated solution of calcium hydroxide into a conical flask. A saturated solution is used because it contains the maximum mass of solute in a given volume of solution.

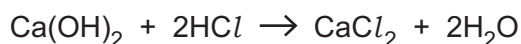
- (i) The uncertainty in using a 25.0 cm^3 pipette is 0.06 cm^3 .

Calculate the percentage uncertainty in using this pipette.

$$(0.06 / 25.0) \times 100$$

percentage uncertainty = ...0.24..... % [1]

- (ii) The student titrates the 25.0 cm^3 of saturated $\text{Ca}(\text{OH})_2$ with hydrochloric acid of concentration 0.100 mol dm^{-3} .



A mean titre of 11.70 cm^3 is obtained.

Calculate the concentration of the saturated calcium hydroxide solution in g dm^{-3} .

$$\text{moles HCl} = 11.70 / 1000 \times 0.100 = 1.17 \times 10^{-3} \text{ mol}$$

$$\text{moles Ca}(\text{OH})_2 = 1.17 \times 10^{-3} / 2 = 5.85 \times 10^{-4} \text{ mol}$$

$$\text{concentration} = 5.85 \times 10^{-4} \times 1000 / 25.0 = 0.0234 \text{ mol dm}^{-3}$$

$$M_r \text{ Ca}(\text{OH})_2 = 40.1 + 2(16.0 + 1.0) = 74.1$$

$$\text{concentration} = 0.0234 \times 74.1 = 1.73 \text{ g dm}^{-3}$$

concentration = ...1.73..... g dm^{-3} [4]

- (e) The titration described in part (d) is repeated with 25.0 cm^3 of saturated barium hydroxide solution.

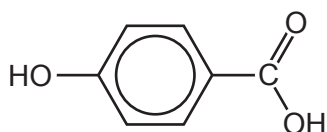
Suggest how the mean titre of 0.100 mol dm^{-3} hydrochloric acid would differ from that for the saturated calcium hydroxide solution. Explain your answer.

The mean titre would be greater (larger than 11.70 cm^3), because barium hydroxide is more soluble than calcium hydroxide (solubility increases down Group 2), so there are more OH^- ions in 25.0 cm^3 [1]

- 3 Parabens are compounds used as preservatives in some cosmetics.

A paraben can be made from the reaction between 4-hydroxybenzoic acid and ethanoic anhydride.

- (a) 4-hydroxybenzoic acid has the following structural formula.



4-hydroxybenzoic acid reacts with both sodium hydroxide and sodium carbonate solutions.

The reaction with sodium hydroxide gives a compound with the molecular formula $C_7H_4O_3Na_2$.

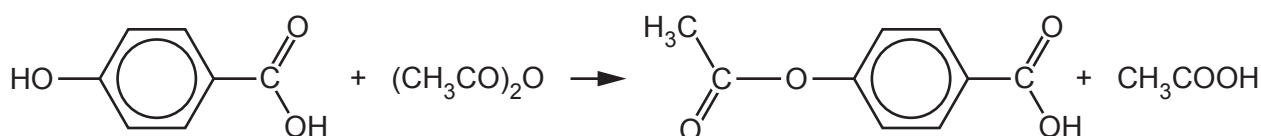
The reaction with sodium carbonate gives a compound with the molecular formula $C_7H_5O_3Na$.

Use acid-base chemistry to explain these observations and include the structural formula for the organic product of each reaction.

NaOH is a strong base, so it reacts with both the phenol OH and the carboxyl COOH groups (both lose H^+), giving $NaOC_6H_4COONa$. Sodium carbonate only reacts with the carboxyl group, giving HOC_6H_4COONa . This is because the carboxyl group is more acidic than the phenol group; carbonate is not a strong enough base to remove H^+ from the phenol.

[3]

- (b) A student makes 4-acetoxybenzoic acid in the laboratory by heating 4-hydroxybenzoic acid and ethanoic anhydride under reflux.



4-hydroxybenzoic acid

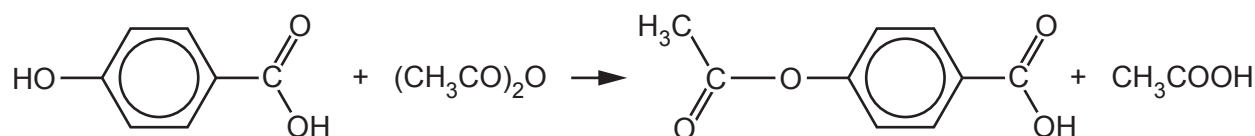
4-acetoxybenzoic acid

- (i) Explain why the heating is carried out under reflux.

To heat for a long time without loss of reactants or products by evaporation; the vapour condenses and returns to the flask.

[1]

The reaction from (b) is shown again here.



4-hydroxybenzoic acid
 $M_r = 138$

4-acetoxybenzoic acid
 $M_r = 180$

- (ii) The student reacts 3.5 g of 4-hydroxybenzoic acid with an excess of ethanoic anhydride. After purifying the crude product the student obtains 2.8 g of 4-acetoxybenzoic acid.

Calculate the percentage yield of 4-acetoxybenzoic acid.

Give your answer to an **appropriate** number of significant figures.

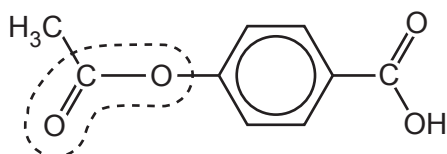
$$\text{moles 4-hydroxybenzoic acid} = 3.5 / 138 = 0.0254 \text{ mol}$$

$$\text{theoretical mass of product} = (3.5 / 138) \times 180 = 4.57 \text{ g}$$

$$\text{percentage yield} = 2.8 / 4.57 \times 100 = 61\% \text{ (2 s.f.)}$$

percentage yield = ...61..... % [3]

- (c) Give the name of the functional group enclosed by the dashed line in the structure of 4-acetoxybenzoic acid.



Ester..... [1]

- (d) 4-acetoxybenzoic acid has a melting point of 193 °C.

A student explains the high melting point as follows:

- Oxygen is more electronegative than carbon so the carbon-oxygen double bond will be polar.
- Strong permanent dipole-permanent dipole attractions occur between $C^{\delta+}$ and $O^{\delta-}$ atoms at either end of neighbouring molecules.

Discuss the student's statements, giving the correct chemistry where necessary.

The first statement is correct: oxygen is more electronegative than carbon, so the C=O bond is polar ($C^{\delta+}$, $O^{\delta-}$).

The second statement is wrong: permanent dipole-permanent dipole attractions do occur between the C=O groups, but they are not strong; they are not the strongest intermolecular bonds here.

The high melting point is due to the stronger hydrogen bonds between the carboxyl ($COOH$) groups of neighbouring molecules.

[3]

- (e) Describe a simple test-tube reaction that would distinguish between 4-hydroxybenzoic acid and 4-acetoxybenzoic acid.

Add neutral iron(III) chloride solution: a purple colour forms with 4-hydroxybenzoic acid only (it has a phenol group).

[1]

- (f) 4-acetoxybenzoic acid is much more soluble in hot ethanol than cold ethanol.

Using this information, describe how to obtain a pure dry sample of 4-acetoxybenzoic acid from the crude product.

Dissolve the crude product in the minimum volume of hot ethanol.

Filter the hot solution to remove any insoluble impurities.

Allow the hot solution to cool so that crystals of 4-acetoxybenzoic acid form; soluble impurities stay in solution.

Filter off the crystals (using reduced pressure / Buchner filtration).

Wash the crystals with a little cold ethanol and dry them (in a desiccator or low oven).

[4]

(g)* The hydrolysis of parabens into 4-hydroxybenzoic acid may occur in slightly acidic or slightly alkaline household wastewater.

Some students investigate this hydrolysis. They make 4 solutions:

- a slightly alkaline solution of 4-acetoxybenzoic acid, **X**
- a slightly acidic solution of 4-acetoxybenzoic acid, **Y**
- a solution of pure 4-acetoxybenzoic acid, **P**
- a solution of pure 4-hydroxybenzoic acid, **B**

They run thin layer chromatograms of **X**, **P** and **B** (Fig. 3.1) and **Y**, **P** and **B** (Fig. 3.2).

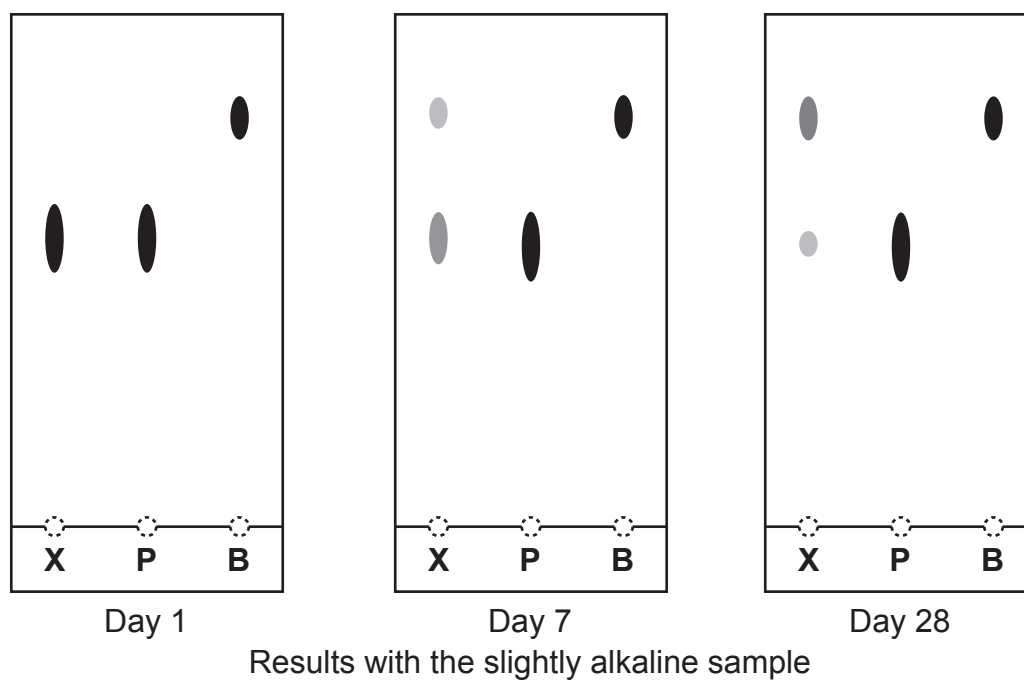


Fig. 3.1

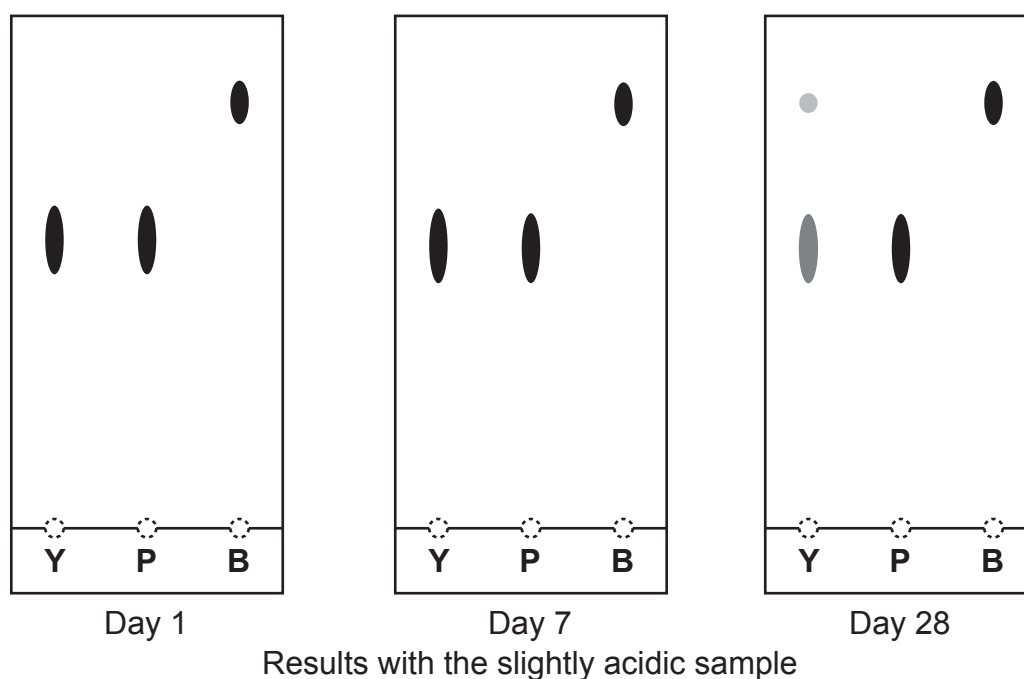


Fig. 3.2

The chromatograms shown in **Fig. 3.1** and **Fig. 3.2** are for samples taken from the 4 solutions on day 1, day 7 and day 28.

Describe how to produce one of these thin layer chromatograms and explain what all the results show. [6]

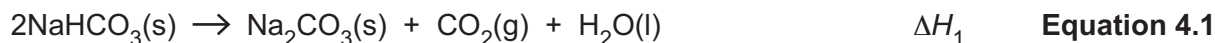
Method: draw a pencil line (baseline) about 1 cm above the bottom of a TLC plate. Use a capillary tube to put small spots of the sample (X or Y), pure P and pure B side by side on the line. Place the plate in a beaker containing a little solvent, with the pencil line above the solvent level, and cover the beaker (with a watch glass). When the solvent front is near the top of the plate, remove it, mark how far the solvent has reached and allow the plate to dry. Locate the spots under a UV lamp or with iodine, and compare the heights (R_f values) of the spots from the sample with those of P and B. Alkaline results (Fig. 3.1): on day 1, X gives only a spot level with P, so no hydrolysis. By day 7, X also has a faint spot level with B, so some 4-acetoxybenzoic acid (paraben) has broken down to 4-hydroxybenzoic acid after 1 week. By day 28 the P spot in X is fainter and the B spot darker, so even more has hydrolysed after 1 month. Acidic results (Fig. 3.2): on days 1 and 7, Y gives only the P spot, so no B

Additional answer space if required

was produced after 1 week. By day 28 there is a faint B spot and the P spot is slightly fainter, so some hydrolysis has occurred after 1 month. So hydrolysis is faster in alkaline conditions than in acidic conditions.

14
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- 4 Sodium hydrogencarbonate is used in baking powder. When it is heated above about 80 °C it begins to break down as shown in **equation 4.1**.



The enthalpy change for the thermal decomposition of sodium hydrogencarbonate, ΔH_1 , is difficult to determine directly by experiment.

Instead the enthalpy change for the reaction is determined indirectly using Hess' law.

The enthalpy changes ΔH_2 and ΔH_3 are determined separately.



- (a) Suggest why it is difficult to measure ΔH_1 directly.

Thermal decomposition requires heating, so the temperature change cannot be measured (and other reactions may occur). [1]

- (b) A student does an experiment to measure ΔH_2 .

The student adds 7.50×10^{-2} mol of NaHCO_3 to 50.00 cm³ (an excess) of 2.00 mol dm⁻³ HCl. The temperature **decreases** by 7.50 °C.

Use this data to calculate ΔH_2 in kJ per mol of NaHCO_3 .

Assume the density and the specific heat capacity of the solution are the same as those of water.

$$q = mc\Delta T = 50.00 \times 4.18 \times 7.50 = 1567.5 \text{ J} = 1.5675 \text{ kJ}$$

$$\Delta H_2 = +1.5675 / 7.50 \times 10^{-2} = +20.9 \text{ kJ mol}^{-1}$$

(temperature fell, so endothermic, positive sign)

$$\Delta H_2 = \dots\dots\dots +20.9 \dots\dots\dots \text{ kJ mol}^{-1} \text{ [2]}$$

(c)* Another student does an experiment to measure ΔH_3 .

The student uses a measuring cylinder to place 50 cm^3 (an excess) of $2.00\text{ mol dm}^{-3}\text{ HCl}$ into a glass beaker.

The student measures the temperature of the acid using a thermometer, taking readings to the nearest degree $^{\circ}\text{C}$.

3.0 g of Na_2CO_3 is added to the acid. The temperature increases slowly and the student records the temperature every minute.

The student uses the highest temperature reached (an increase of 5°C) to calculate ΔH_3 .

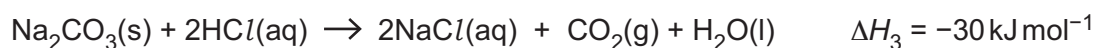
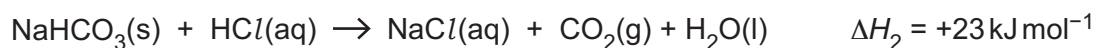
The student wants to repeat the experiment to get a more accurate measurement of ΔH_3 .

Describe how measurement uncertainties and the effects of 'heat loss' can be reduced in the experiment. [6]

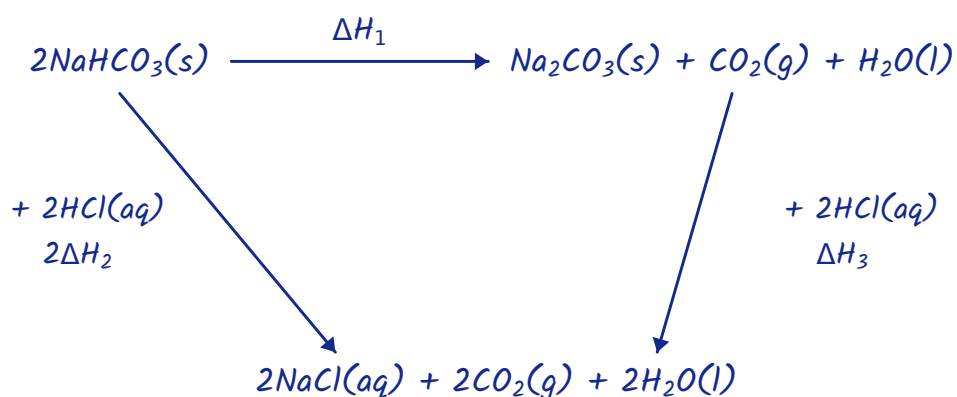
Measurement uncertainty: measure the acid with a 50.0 cm^3 pipette (or burette) instead of a measuring cylinder.
Use a thermometer reading to 0.1°C (or 0.5°C) instead of the nearest degree, so the percentage uncertainty in the 5°C rise is smaller.
Weigh the Na_2CO_3 on a balance reading to 0.01 g .
Heat losses: use a polystyrene cup (insulated) instead of a glass beaker, which conducts heat away, and put a loose-fitting lid on it (loose because CO_2 gas is evolved). Stir throughout so the temperature is even.
Graphical method: record the temperature for a few minutes before adding the Na_2CO_3 , then every half minute after adding it, continuing until the temperature has peaked and starts to fall again.
Plot temperature against time and extrapolate the cooling line back to the time when the reactants were mixed. Read off the theoretical maximum temperature change there; this corrects for heat lost while the temperature rose slowly.

Additional answer space if required

- (d) In separate accurately performed experiments the following enthalpy changes were determined.



Draw a Hess' law enthalpy cycle and use these values for ΔH_2 and ΔH_3 to calculate a value for ΔH_1 .



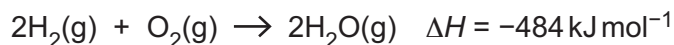
$$\Delta H_1 = 2\Delta H_2 - \Delta H_3$$

$$\Delta H_1 = 2(+23) - (-30)$$

$$\Delta H_1 = +76 \text{ kJ mol}^{-1}$$

enthalpy change $\Delta H_1 = \dots\dots\dots +76 \dots\dots\dots \text{ kJ mol}^{-1}$ [4]

- (e) Bond enthalpies can be used in some calculations involving ΔH values.
Use the data below to calculate a value for the bond enthalpy of the H–O bond.



Bond	Bond enthalpy / kJ mol^{-1}
H–H	+436
O=O	+498

$$\text{bonds broken: } 2(\text{H-H}) + (\text{O=O}) = 2(436) + 498 = 1370 \text{ kJ}$$

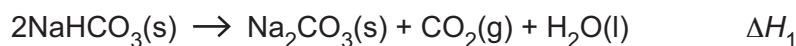
$$\text{bonds made: } 4(\text{O-H})$$

$$\Delta H = 1370 - 4(\text{O-H}) = -484$$

$$4(\text{O-H}) = 1854, \text{ so } \text{O-H} = +463.5 \text{ kJ mol}^{-1}$$

$$\text{bond enthalpy of H-O} = \dots\dots\dots +463.5 \dots\dots\dots \text{ kJ mol}^{-1} \quad [2]$$

- (f) Why can bond enthalpies **not** be used to estimate ΔH_1 ?



NaHCO₃ and Na₂CO₃ are ionic, so not all the bonds are covalent (bond enthalpies only apply to covalent bonds). [1]

END OF QUESTION PAPER

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